

**PATENT**

#19 1/23/03  
2)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Application No.: 09/775,069  
Filing Date: February 1, 2001  
Applicant: G. Mourou  
Group Art Unit: 1725  
Examiner: G. Evans  
Title: METHOD FOR CONTROLLING CONFIGURATION OF  
LASER INDUCED BREAKDOWN AND ABLATION  
Attorney Docket: 2115D-000939/DVD

RECEIVED  
JAN 13 2003  
TECHNOLOGY CENTER 1700

---

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**DECLARATION EXHIBITS**

Sir:

An Amendment was filed for the above-identified case on November 15, 2002, in response to an Office Action dated July 17, 2002. The Amendment included Declarations filed under 37 CFR 1.131 and signed by the inventors. The Declarations referred to Exhibits 1 through 6. Exhibits 1 through 6 were inadvertently absent from the Amendment as filed.

The undersigned contacted Examiner Geoffrey Evans by telephone on January 10, 2003 regarding the absence of the Exhibits from the November 15, 2002 Amendment. Examiner Evans agreed to accept personal delivery of the Exhibits on Monday, January 13, 2003.

Attached hereto is a copy of Exhibits 1 through 6. Applicant thanks the Examiner for his consideration and looks forward to favorable consideration of the November 15, 2002 Amendment.

The Commissioner is hereby authorized to charge any additional fees that may be required under 37 CFR 1.16 or 1.17 to Deposit Account No. 08-0750. A duplicate copy of this form is enclosed.

If the Examiner has any questions or requires further information, the Examiner is invited to telephone the undersigned at (248) 641-1600.

Respectfully submitted,

Dated: Jan. 13, 2003

By: 

Ryan McCarthy  
Reg. No. 50,636

HARNESS, DICKEY & PIERCE, P.L.C.  
P.O. Box 828  
Bloomfield Hills, Michigan 48303  
(248) 641-1600

## **LIST OF EXHIBITS**

- Exhibit 1      a) Sub-Wavelength Micro-Machining by Ultrafast Laser Ablation;  
                  b) Laser-Induced Breakdown by Impact Ionization in SiO<sub>2</sub> with  
                      Pulse-widths from 7 ns to 150 fs; and  
                  c) Damage Threshold as a Function of Pulse Duration in  
                      Biological Tissue.
- Exhibit 2      Copy of letter dated March 31, 1994 from Linda Deschere  
                  transmitting a draft patent application
- Exhibit 3      Copy of the facsimile cover dated March 31, 1994 from Peter  
                  Pronko to Linda Deschere transmitting inventor, Peter Pronko's  
                  comments
- Exhibit 4      Copy of the facsimile cover dated April 5, 1994 from Jeff Squier and  
                  Gerard Mourou to Linda Deschere transmitting comments of  
                  inventors, Jeff Squier and Gerard Mourou
- Exhibit 5      Copy of the letter dated April 6, 1994 from Linda Deschere  
                  transmitting a subsequent draft patent application
- Exhibit 6      Copy of facsimile cover dated April 7, 1994 from Gerard Mourou to  
                  Linda Deschere transmitting comments

## Sub-Wavelength Micro-Machining by Ultrafast Laser Ablation

S. K. Dutta, P. P. Pronko, and G. Mourou  
*Center for Ultrafast Optical Science*  
Dept. of Electrical Engineering  
and Computer Science  
*University of Michigan*  
Ann Arbor, MI 48109  
313-763-4875

### Introduction

Current laser machining using nano-second pulses cannot produce features smaller than the spot size due to thermal interactions with the material [1]. This paper presents arguments and a demonstration that by using femtosecond pulses the spatial resolution of the ablation/machining process can be considerably less than the wavelength of the laser radiation used to produce it. We have produced laser ablated holes with diameters of 10% the laser beam spot size.

### Theory

The basic premise for explaining our observations is found in (a) the solid state thermal diffusion length for the deposited optical energy, (b) the absorption depth for the optical radiation and (c) the time necessary for a vapor to develop at the surface of the material.

For ultrafast pulses in metals the thermal diffusion length,  $l_{th} = (Dt)^{1/2}$  (where  $D$  is the thermal diffusivity and  $t$  the pulse time), is significantly smaller than the absorption depth ( $1/a$ ), where  $a$  is the absorption coefficient for the radiation. For our experimental conditions with wavelength of 800 nm and 200 fs pulses on gold, the absorption depth is 275 Å with a diffusion length of 50 Å. In the case of nanosecond pulses the diffusion length, which is on the order of 10  $\mu\text{m}$ , is much longer than the absorption depth, resulting in thermal diffusion being the limiting factor in feature size resolution. Empirical evidence for the existence of these two regimes is exhibited in Figure 1. Here, both experimental [2] and theoretical [3] ablation thresholds are plotted as a function of pulse width. An arrow at approximately 7 picoseconds delineates the point at which the thermal diffusion length ( $l_{th}$ ) is equal to the absorption depth ( $1/a$ ). It is clear from the figure that this is the point at which the ablation threshold transitions from a slowly varying or nearly constant value as a function of pulse width to one that is dramatically dependent on pulse time. In further support of these arguments, it has been demonstrated [4] that the electron thermalization time for laser deposited energy in gold is on the order of, or less than, 500 fs and the electron-lattice interaction time is 1 ps.

The consequences of this for ultrafast laser pulses is that the energy is contained within the beam spot. In fact for energies at or near the threshold for ablation, the spatial profile of the laser beam will determine the size and shape of the region being ablated.

We have performed an experiment to measure the amount of recombination light produced as a function of the fluence impinging on a gold film. The technique involved is explained in detail in a similar study based on transparent materials [5]. We take the intensity of the light to be proportional to the amount of material ablated. In Figure 2, the material removed is plotted as a function of fluence. A well defined threshold fluence is observed at which material removal is initiated. It is expected that by having only a small fraction of the gaussian beam where the fluence is greater than the threshold, the ablated region can be restricted to this small area. In Figure 2,  $R_a$  is the radial position on the beam where the fluence is at threshold. Ablation, then, occurs only within a radius  $R_a$ . It

is evident that by properly choosing the incident fluence, the ablated spot can in principle be smaller than the spot size,  $R_s$ . Although the data for a 150 fs pulse is shown, this threshold behavior is exhibited in a wide range of pulse widths. However, sub spot size ablation is not possible in the longer pulse regimes, due to the dominance of thermal diffusion.

### Experiment

Our laser source is a 800 nm Ti:Sapphire oscillator whose pulses are stretched by a grating pair, amplified in a regenerative amplifier operating at 1 kHz, and finally recompressed by another grating pair. We can obtain pulse widths from 7 ns to 100 fs. The beam is focused with a 10x objective, implying a theoretical spot size of 3.0  $\mu\text{m}$ . Figure 3 shows an SEM photo-micrograph of ablated holes obtained in a silver film on glass, using a pulse width of 200 fs and a pulse energy of 30 nJ (fluence of 0.4 J/cm<sup>2</sup>). Two holes of diameter approximately 0.3  $\mu\text{m}$  are clearly visible. Similar results have been obtained in aluminum.

These results suggest that by, producing a smaller spot size which is a function of numerical aperture and wavelength, even smaller holes can be machined. We have demonstrated the ability to generate the fourth harmonic (200 nm) using a nonlinear crystal. Thus by using a stronger objective lens along with the 200 nm light, holes with diameters of 200 angstroms could in principle be formed.

### Conclusion

It has been demonstrated that sub-wavelength holes can be machined into metal surfaces using femtosecond laser pulses. The effect is physically understood in terms of the thermal diffusion length, over the time period of the pulse deposition, being less than the absorption depth of the incident radiation. The interpretation is further based on the hole diameter being determined by the lateral gaussian distribution of the pulse in relation to the threshold for vaporization and ablation.

### References

1. James Golden, Laser Focus World, June 1992, pp. 75-88.
2. S. K. Dutta, D. Du, J. Squier, P. P. Pronko and R. K. Singh, OSA/IEEE Conference on Lasers and Electro-Optics (CLEO), May 1994 and Bulletin of the American Physical Society, March 1994.
3. Numerical computer code - "Simulation of Laser Interaction with Matter" (SLIM) by R. K. Singh and J. Viatella, University of Florida.
4. C.K. Sun, F. Vallee, L. Acioli, E. P. Ippen, and J. G. Fujimoto, Phys. Rev. B, 48, 12-365 (1993).
5. D. Du *et. al.* , Appl. Phys. Lett., to be published.

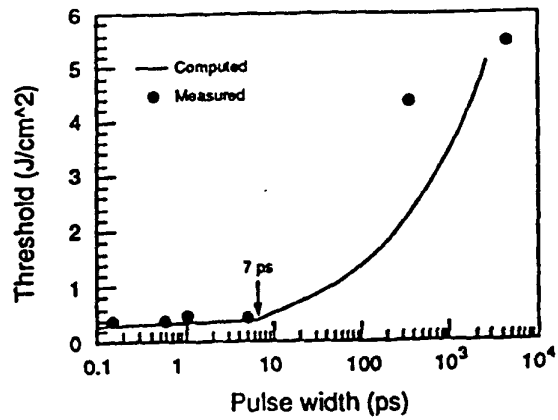


Figure 1. Ablation threshold vs. pulsewidth in gold.

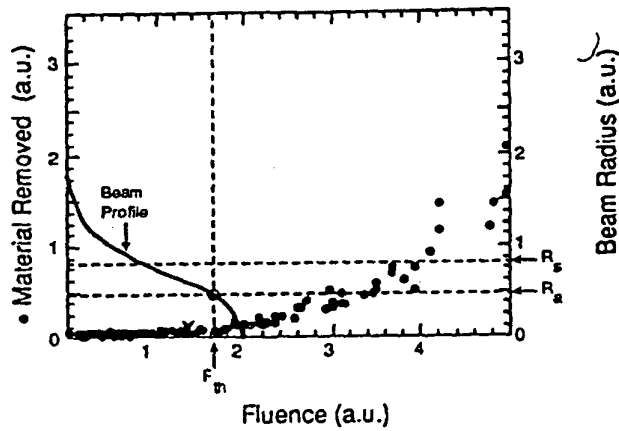


Figure 2. Sub spot size machining at ablation threshold in gold.  $F_{th}$  is the threshold fluence needed to initiate material removal.  $R_s$  is the spot size of the incident beam and  $R_a$  is the radius of the ablated hole.



Figure 3. SEM view of two  $0.3 \mu\text{m}$  holes machined in silver film.

# Laser-Induced Breakdown by Impact Ionization in SiO<sub>2</sub> with Pulse-widths from 7 ns to 150 fs

D. Du, X. Liu, G. Korn, J. Squier, and G. Mourou

*Center for Ultrafast Optical Science, University of Michigan, Ann Arbor, MI 48109-2099*

## Abstract

Results of laser-induced breakdown experiments in fused silica (SiO<sub>2</sub>) employing 150 fs – 7 ns, 780 nm laser pulses are reported. The avalanche ionization mechanism is found to dominate over the entire pulse-width range. Fluence breakdown threshold does not follow the scaling of  $F_{th} \sim \sqrt{\tau_p}$ , when pulses are shorter than 10 ps. The impact ionization coefficient of SiO<sub>2</sub> is measured up to  $\sim 3 \times 10^8$  V/cm. The relative role of photoionization in breakdown for ultrashort pulses is discussed.

Typeset using REVTeX

Laser-induced breakdown (LIB) in optically transparent materials has been studied extensively since the laser was invented in the 1960's [1]– [4]. LIB mechanisms have been investigated for laser pulse-widths down to tens of picoseconds. LIB remains an important topic because of its role in a wide range of high-power laser applications, where damage to optical components due to LIB often is the ultimate restriction on system performance. Increasingly, high laser power is achieved with moderate amount of energy ( $\sim$  joules) by reducing the pulse-width from picoseconds to femtoseconds. Our present work is to investigate LIB in this important regime.

It is a well-established fact that the breakdown threshold depends on the pulse-width of the laser pulses. An empirical scaling law of the fluence breakdown threshold for longer pulses ( $\tau_p > 30$  ps) exists [6]:  $F_{th} \propto \sqrt{\tau_p}$ . Until recently, the shortest pulses available for LIB studies were in the range of tens of picoseconds. However, new techniques in ultrashort laser pulse generation and amplification, such as the chirped-pulse amplification (CPA) [7], have pushed the available pulse-widths to femtosecond regime. More importantly, CPA readily allows one to vary the laser pulse-width continuously — up to hundreds of picoseconds — from a single laser system based on this principle. The setup of an LIB experiment using such a laser can therefore have a wide range of laser pulse-widths, without changing other important parameters, such as the focusing of the pulse onto the sample.

We have performed a series of experiments to determine the LIB threshold as a function of laser pulse-width between 150 fs – 7 ns, using a CPA laser system. The short-pulse laser used in our experiment was a 10-Hz Ti:sapphire oscillator-amplifier system based on the CPA technique. The laser pulse was focused by an  $f = 25$  cm lens inside the  $\text{SiO}_2$  sample. The Rayleigh length of the focused beam is  $\sim 2$  mm. The focused spot-size was measured in-situ by a microscope objective lens. The measured spot-size (FWHM) was  $26 \mu\text{m}$  in a gaussian mode. The fused silica samples were made from Corning 7940, with a thickness of 0.15 mm. They were optically polished on both sides with a scratch/dig of 20-10. Each sample was cleaned by methanol before the experiment. Thin samples were used in order to avoid the complications of self-focusing of the laser pulses in the bulk. The  $\text{SiO}_2$  sample



was mounted on a computer-controlled motorized X-Y translation stage. Each location on the sample was illuminated by the laser only once.

Two diagnostics were used to determine the breakdown threshold  $F_{th}$ . First, the plasma emission from the focal region was collected by a lens to a photomultiplier tube with appropriate filters. Second, the change of transmission through the sample was measured with an energy meter. Visual inspection was performed to confirm the breakdown at nanosecond pulse duration. Fig. 1 shows typical plasma emission and transmitted light signal vs. incident laser energy plots, at a laser pulse-width of  $\tau_p = 300$  fs. It is worth noting that the transmission changed slowly at around  $F_{th}$ . This can be explained by the temporal and spatial behavior of the breakdown with ultrashort pulses. Due to the spatial variation of the intensity, the breakdown will reach threshold at the center of the focus, and because of the short pulse duration, the generated plasma will stay localized. The decrease in transmitted light is due to the reflection, scattering, and absorption by the plasma. By assuming a gaussian profile in both time and space for the laser intensity, and further assuming that the avalanche takes the entire pulse duration to reach threshold, one can show that the transmitted laser energy  $U_t$  as a function of the input energy  $U$  is given by

$$U_t = \begin{cases} kU, & U \leq U_{th} \\ kU_{th} [1 + \ln(U/U_{th})], & U > U_{th} \end{cases} \quad (1)$$

where  $k$  is the linear transmission coefficient. The solid curve in Fig. 1 is plotted using Eq. (1), with  $U_{th}$  as a fitting parameter. In contrast, breakdown caused by nanosecond laser pulses cuts off the transmitted beam near the peak of the pulses [8], indicating a different temporal and spatial behavior.

Figure 2 shows the fluence breakdown threshold  $F_{th}$  as a function of laser pulse-width. From 7 ns to about 10 ps, the breakdown threshold follows the scaling law of  $F_{th} \propto \sqrt{\tau_p}$ . Breakdown thresholds from earlier work in this pulse width regime are also shown as a comparison – it can be seen that our data is consistent with earlier work. However, when the pulse-width becomes shorter than a few picoseconds, the threshold starts to increase. This increase at shorter pulse-widths may come as a surprise at first, but it still falls into

the regime of an avalanche dominated process at high field strength, as we will show below.

The ionization process of a solid illuminated by an intense laser pulse can be described by the general equation

$$\frac{dn_e(t)}{dt} = \eta(E)n_e(t) + \left(\frac{dn_e(t)}{dt}\right)_{PI} - \left(\frac{dn_e(t)}{dt}\right)_{loss}, \quad (2)$$

where  $n_e(t)$  is the free electron (plasma) density,  $\eta(E)$  is the avalanche coefficient, and  $E$  is the electric field strength. The second term on the right hand side is the photoionization contribution, and the third term is the loss due to electron diffusion, recombination, etc. When the pulse-width is in the picosecond regime, the loss of the electron is negligible during the duration of the short pulse.

Photoionization contribution can be estimated by the tunneling rate [9]. For short pulses,  $E \sim 10^8$  V/cm, the tunneling rate is estimated to be  $w \sim 4 \times 10^9$  sec<sup>-1</sup>, which is small compared to that of avalanche, which is derived below. However, photoionization can provide the initial electrons needed for the avalanche processes at short pulse-widths. For example, our data shows at 1 ps, the rms field threshold is about  $5 \times 10^7$  V/cm. The field will reach a value of  $3.5 \times 10^7$  V/cm (rms) at 0.5 ps before the peak of the pulse, and  $w \sim 100$  sec<sup>-1</sup>. During a  $\Delta t \sim 100$  fs period the electron density can reach  $n_e \sim n_i[1 - \exp(-w\Delta t)] \sim 10^{11}$  cm<sup>-3</sup>, where  $n_i \sim 10^{22}$  is the total initial valence band electron density.

Neglecting the last two terms in Eq. (2), we then have the case of an electron avalanche process, with impact ionization by primary electrons driven by the laser field. The electron density is then given by  $n_e(t) = n_0 \times \exp(\eta(E)t)$ , where  $n_0$  is the initial free electron density. These initial electrons may be generated through thermal ionization of shallow traps or photoionization. When assisted by photoionization at short pulse regime, the breakdown is more deterministic, as contrary to that of nanosecond pulses, where the breakdown is more statistical [10]. According to the commonly accepted condition that breakdown occurs when the electron density exceeds  $n_{th} \simeq 10^{18}$  cm<sup>-3</sup> and an initial density of  $n_0 \simeq 10^{10}$  cm<sup>-3</sup>, the breakdown condition is then given by  $\eta\tau_p \simeq 18$  [5], [10]. For our experiment, it is more appropriate to use  $n_{th} \simeq 1.6 \times 10^{21}$  cm<sup>-3</sup>, the plasma critical density, hence the threshold

is reached when  $\eta\tau_p \simeq 30$ . There is some arbitrariness in the definition of plasma density relating to the breakdown threshold. However, the particular choice of plasma density does not change the dependence of threshold as function of pulse duration (the scaling law).

In our experiment, the applied electric field is on the order of a few tens of MV/cm and higher. Under such a high field, the electrons have an average energy of  $\sim 5$  eV, and the electron collision time  $\tau$  is less than 0.4 fs for electrons with energy  $U \geq 5 - 6$  eV [11]. Electrons will make more than one collision during one period of the electric oscillation. Hence the electric field is essentially a dc field to those high energy electrons. The breakdown field at optical frequencies has been shown to correspond to dc breakdown field by the relationship [2]  $E_{th}^{rms}(\omega) = E_{th}^{dc}(1 + \omega^2\tau^2)^{1/2}$ , where  $\omega$  is the optical frequency and  $\tau$  is the collision time.

In dc breakdown, the ionization rate per unit length,  $\alpha$ , is used to describe the avalanche process, with  $\eta = \alpha(E)v_{drift}$ , where  $v_{drift}$  is the drift velocity of electrons. When the electric field is as high as a few MV/cm, the drift velocity of free electrons is saturated and independent of the laser electric field,  $v_{drift} \simeq 2 \times 10^7$  cm/s [12].

Thornber [13] has derived an expression for  $\alpha(E)$  which is applicable for all electric field strengths, which is essential when comparing to our experimental data. The ionization rate per unit length of an electron is just  $eE/U_i$  times the probability,  $P(E)$ , that the electron has an energy  $\geq U_i$ , or  $\alpha(E) = (eE/U_i)P(E)$ . We denote  $E_{kT}$ ,  $E_p$ , and  $E_i$  as threshold fields for electrons to overcome the decelerating effects of thermal, phonon, and ionization scattering, respectively. When the electric field is negligible,  $E < E_{kT}$ , so the distribution is essentially thermal,  $P(E)$  is simply  $\exp(-U_i/kT)$ . Shockley [14] showed  $P(E) \sim \exp(-\text{const}/E)$  for  $E_{kT} < E < E_p$ . Wolff [15] found  $P(E) \sim \exp(-\text{const}/E^2)$  at higher fields ( $E > E_p$ ). Thornber combined the three cases and gave an expression that satisfies both low and high field limits:

$$\alpha(E) = \frac{eE}{U_i} \exp\left(-\frac{E_i}{E(1 + E/E_p) + E_{kT}}\right). \quad (3)$$

This leads to  $F_{th} \propto E^2\tau_p \sim 1/\tau_p$ , i.e., the fluence threshold will increase for ultrashort laser

pulses when  $E > \sqrt{E_p E_i}$  is satisfied.

In Fig. 3, we plot  $\alpha$  as a function of the electric field,  $E$ . From our experimental data, we calculate  $\alpha$  according to  $\eta\tau_p = 30$  and  $\eta = \alpha v_{\text{drift}}$ . The solid curve is calculated from Eq. (3), using  $E_i = 30$  MV/cm,  $E_p = 3.2$  MV/cm, and  $E_{kT} = 0.01$  MV/cm. These parameters are calculated from  $U = eEl$ , where  $U$  is the appropriate thermal, phonon, and ionization energy, and  $l$  is the corresponding energy relaxation length ( $l_{kT} = l_p \sim 5$  Å, the atomic spacing, and  $l_i \simeq 30$  Å, see [16] and the references there in). It shows the same saturation as the experimental data. The dashed line is corrected by a factor of 1.7, which results in an excellent fit with the experimental data. This factor of 1.7 is of relatively minor importance, as it can be due to a systematic correction, or because breakdown occurred on the surface first, which could have a lower threshold. The uncertainty of the saturation value of  $v_{\text{drift}}$  also can be a factor. The most important aspect is that the shape (slope) of the curve given by Eq. (3) provides excellent agreement with the experimental data. This prompts us to conclude that in our experiments, the mechanism of laser-induced breakdown in fused silica, using pulses as short as 150 fs and wavelength at 780 nm, is still dominated by the avalanche process.

In summary, we have investigated the pulse-width dependence of the laser-induced optical breakdown threshold in fused silica with laser pulse-widths over approximately 5 orders of magnitude, from 7 ns to 150 fs. We are able to obtain very good agreement, over the entire pulse-width range, on the ionization rate  $\alpha$  between experiment and impact ionization theory. For picosecond pulses, evidence shows that photoionization is responsible for the initial electron generation. The plasma generated during breakdown with ultrashort pulses remains localized at the threshold, which could provide precise control of the interaction region for material processing and medical laser applications when ultrashort pulses are used. Our study is also relevant to solid-state microelectronics, as the structures become smaller and faster, electron transport properties under high fields and short durations – conditions explored in our experiment – will be increasingly important.

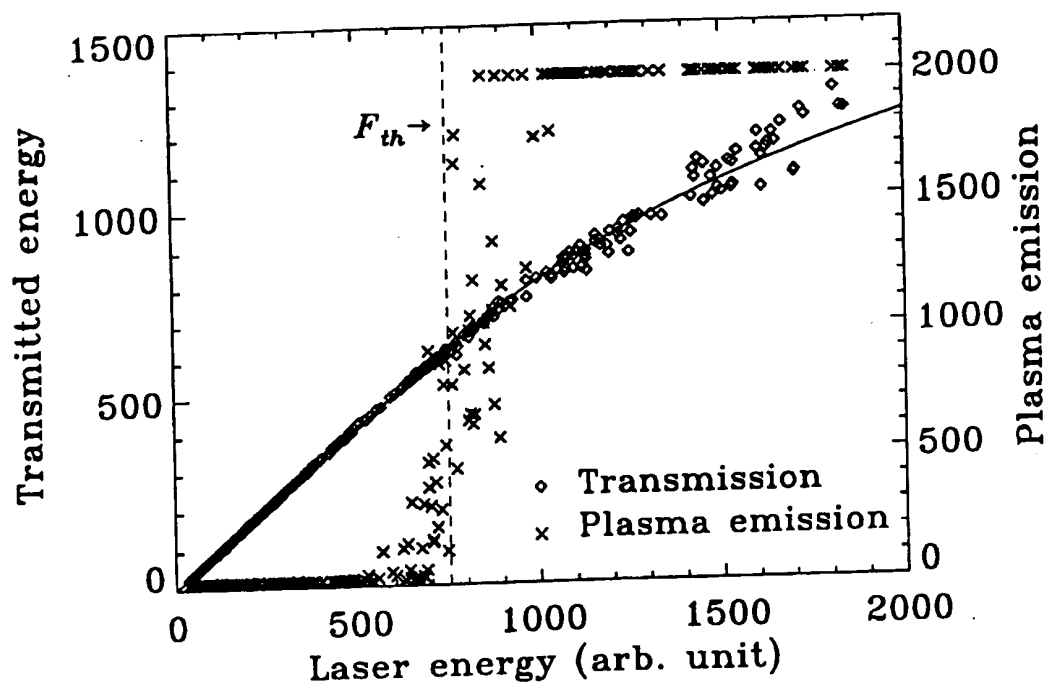
This work was funded by the Office of Naval Research and the National Science Foundation through the Center for Ultrafast Optical Science under STC PHY 8920108. We wish to thank T. Norris for helpful comments and P. Schermerhorn of Corning, Inc., who provided fused silica samples for the experiment.

## REFERENCES

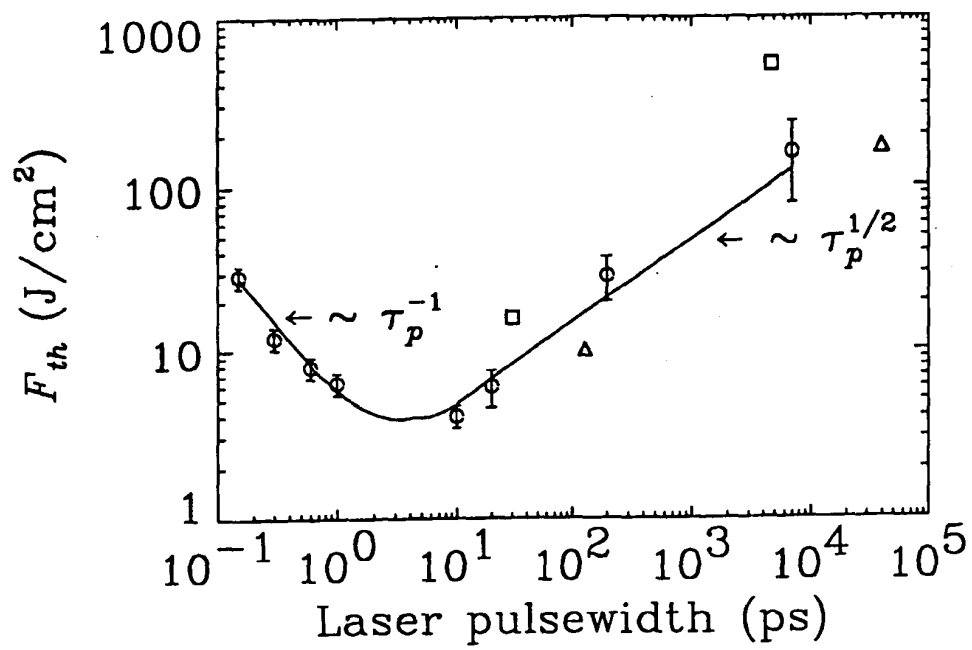
- [1] See the series of Proceedings of the Boulder Damage Symposium: Laser Induced Damage in Optical Materials, 1-24 (1969-92).
- ✓ [2] N. Bloembergen, IEEE J. Quantum Electron. QE-10, 375 (1974).
- [3] W. L. Smith, Opt. Eng. 17, 489-503 (1978).
- [4] S. C. Jones, P. Braunlich, R. T. Casper, Xiao-An Shen, and P. Kelly, Opt. Eng. 28, 1039-1067 (1989).
- [5] E. Yablonovitch and N. Bloembergen, Phys. Rev. Lett. 29, 907 (1972).
- [6] J. R. Bettis, R. A. House II, and A. H. Guenther, in *Laser Induced Damage in Optical Materials: 1976*, NBS Spec. Pub. 462, 338-345 (1976).
- [7] D. Strickland and G. Mourou, Opt. Commun. 56, 219 (1985).
- [8] D. W. Fradin, E. Yablonovitch, and M. Bass, Appl. Opt. 29, 700 (1973).
- [9] M. V. Ammosov, N. B. Delone, and V. P. Krainov, Sov. Phys. JETP 64, 1191 (1986).
- [10] D. Milam, in *Laser-Induced Damage in Optical Materials: 1976*, NBS Spec. Pub. 462, 350-356 (1976).
- [11] M. V. Fischetti, and D. J. DiMaria, Solid-State Electron. 31, 629 (1988).
- [12] R. C. Hughes, Solid-State Electron. 21, 251 (1978).
- [13] K. K. Thornber, J. Appl. Phys. 52, 279 (1981).
- [14] W. Shockley, Czech. J. Phys. B11, 81 (1961).
- [15] P. A. Wolff, Phys. Rev. 95, 1415 (1954).
- [16] D. J. DiMaria and J. R. Abernathey, J. Appl. Phys. 60, 1727 (1986).
- [17] S. Stokowski, D. Milam, and M. Weber, in *Laser-Induced Damage in Optical Materials:*

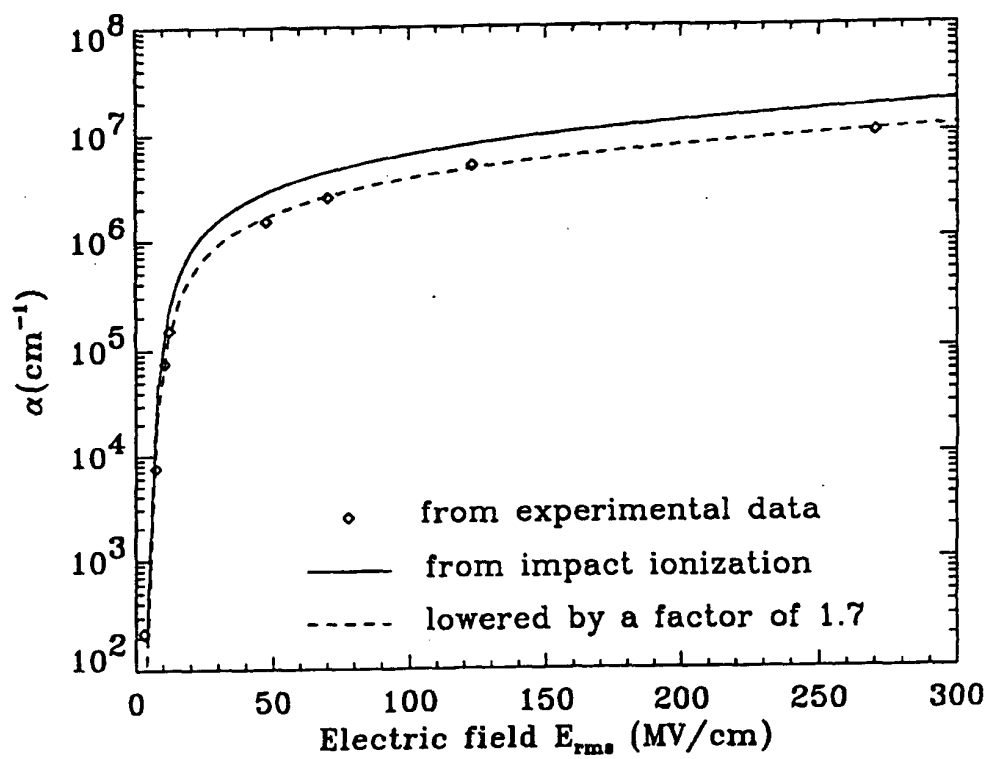
1978, NBS Spec. Pub. 541, 99-108 (1978).

FIGURES









## Figure Captions

FIG. 1. Scattered plasma emission and transmitted laser pulse as a function of incident laser pulse energy.

FIG. 2. Fluence threshold vs. pulse-width. The  $\sqrt{\tau_p}$  scaling holds for pulse-widths down to 10 ps, shown by the solid line. For longer pulse-widths, previously obtained bulk (squares, Smith [3]) and surface (triangles, Stokowski *et al.* [17]) damage data are also shown.

FIG. 3. Impact ionization rate per unit distance  $\alpha$  determined from experiment and theory.

**Damage Threshold as a Function of Pulse Duration in Biological Tissue**

**EXHIBIT 1(c)**

tabbies

USSN  
09/775,069

**Detao Du, Jeff Squier, Xinbing Liu, Gerard Mourou**  
**Center for Ultrafast Optical Science**  
**University of Michigan.**  
**2200 Bonisteel , IST Bldg. Rm. 1006**  
**Ann Arbor, MI 48109-2099**  
**Ph:(313) 763-4875 Fax: (313) 763-4876**

**Geoff Güttmann**  
**Center for Ultrafast Optical Science**  
**University of Michigan.**  
**2200 Bonisteel , IST Bldg. Rm. 1006**  
**Ann Arbor, MI 48109-2099**  
**and**  
**Department of Ophthalmology**  
**Kellogg Eye Center**  
**University of Michigan**  
**1000 Wall Street**  
**Ann, Arbor MI 48105**

**Ron Kurtz, Victor Elnor**  
**Department of Ophthalmology**  
**Kellogg Eye Center**  
**University of Michigan**  
**1000 Wall Street**  
**Ann, Arbor MI 48105**

**Abstract**

**Damage thresholds for corneal tissue are measured as a function of pulse duration, revealing strong departure from previous findings.**

## **Damage Threshold as a Function of Pulse Duration in Biological Tissue**

**Detao Du, Jeff Squier, Xinbing Liu, Gerard Mourou**

**Center for Ultrafast Optical Science**

**University of Michigan.**

**2200 Bonisteel , IST Bldg. Rm. 1006**

**Ann Arbor, MI 48109-2099**

**Ph:(313) 763-4875 Fax: (313) 763-4876**

**Geoff Güttmann**

**Center for Ultrafast Optical Science**

**University of Michigan.**

**2200 Bonisteel , IST Bldg. Rm. 1006**

**Ann Arbor, MI 48109-2099**

**and**

**Department of Ophthalmology**

**Kellogg Eye Center**

**University of Michigan**

**1000 Wall Street**

**Ann, Arbor MI 48105**

**Ron Kurtz, Victor Elnar**

**Department of Ophthalmology**

**Kellogg Eye Center**

**University of Michigan**

**1000 Wall Street**

**Ann, Arbor MI 48105**

### **Summary**

We measured damage thresholds for corneal tissue over a range of pulse durations (from 150 fs - 7 ns) that could not be examined previously with a single laser source, using a Ti:sapphire chirped-pulse amplification (CPA) laser [1]. Our results depart from previous findings [2,3], which had to use multiple laser sources to investigate a similar pulsewidth range.

For ultrashort pulse durations (<10 ps), the primary mechanisms for tissue damage have not been described. For certain applications, such as ophthalmic surgery, collateral damage must be minimized. By understanding the mechanisms and defining the breakdown thresholds for ultrashort pulse durations, we hope to reduce collateral damage for these precision applications.

Laser-induced optical breakdown consists of three general steps: free electron generation and multiplication, plasma heating and material deformation or breakdown. Avalanche ionization and multiphoton ionization are the two processes responsible for the breakdown. The laser-induced breakdown threshold in dielectric material depends on the pulsewidth of the laser pulses. An empirical scaling law of the fluence breakdown threshold as a function of the pulsewidth is given by  $F_{th} \propto \sqrt{\tau_p}$ , or alternatively, the intensity breakdown threshold,  $I_{th} = F_{th}/\tau_p$ . Although this scaling law applies in the pulsewidth regime from nanosecond to tens of picoseconds, recently, we found that the breakdown threshold does not follow the scaling law when laser pulses are shorter than ten picoseconds for SiO<sub>2</sub> [4]. Therefore, a systematic investigation of the breakdown threshold of cornea tissue as a function of the laser pulsewidth should enable us to identify the best operating parameters.

We performed a series of experiments to determine the breakdown threshold of cornea as a function of laser pulsewidth between 150 fs - 7 ns, using a CPA laser system. One advantage of this laser system is the laser pulsewidth can be varied while all other experimental parameters (spot size, wavelength, energy, etc.) remain unchanged. The laser was focused to a spot size (FWHM) of 26  $\mu\text{m}$ . The plasma emission was recorded as a function of pulse energy in order to determine the tissue damage threshold. Histology was also performed to assess tissue damage.

Breakdown thresholds calculated from plasma emission data revealed deviations from the scaling law,  $F_{th} \propto \sqrt{\tau_p}$ . As shown in Figure 1, the scaling law of the fluence threshold is true to about 10 ps, and fails when the pulse shortens to less than a few picoseconds. The standard deviation of breakdown threshold measurements decreased with shorter pulses. Histological analysis reveals more localized ablation with pulses less than 10 ps.

The breakdown threshold for ultrashort pulses (< 10 ps) are less than longer pulses and have smaller standard deviations. The reduced collateral damage caused by ultrashort laser pulses show that these systems may have a future in ophthalmic and other precision surgical procedures.

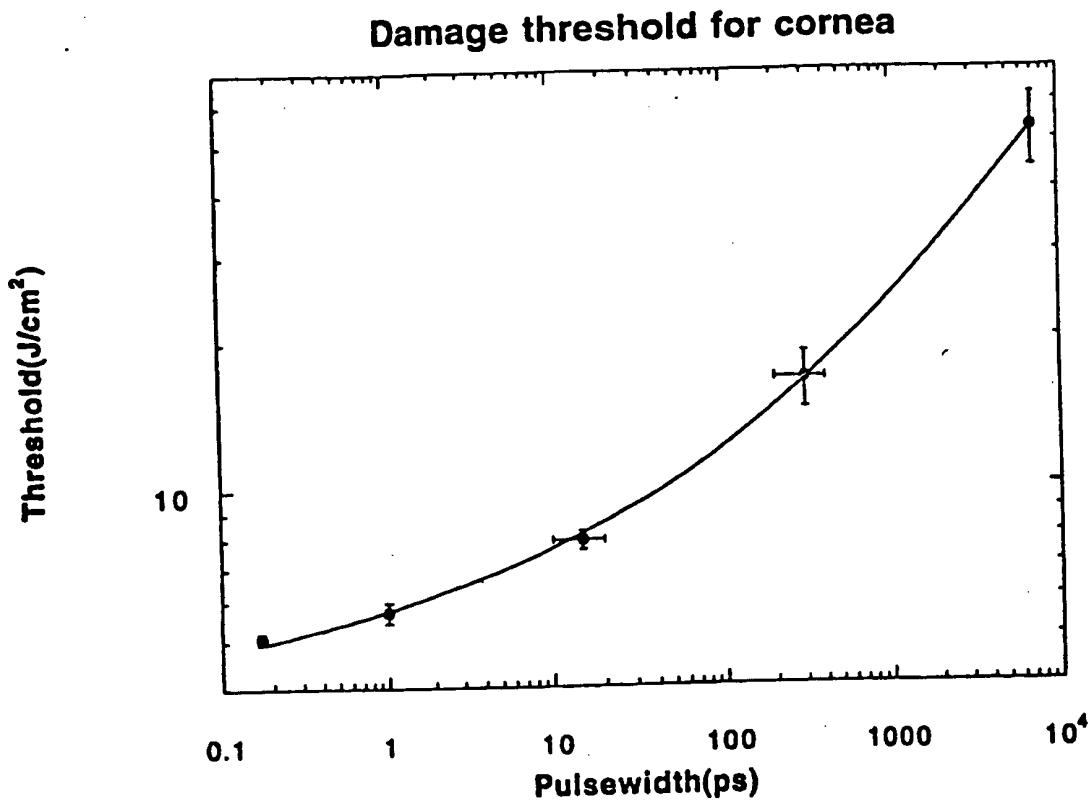


Figure 1. Damage threshold of cornea as a function of pulse duration.

This work was partially supported by the National Science Foundation under STC PHY 8920108 and the Midwest Eye Bank and Transplantation Centers.

- [1] J. Squier, F. Salin, G. Mourou, *Opt. Lett.* **16**, 324
- [2] D. Stern, R. Schoenkin, C. Puliafito, E. Dobi, R. Birngraber, J. Fujimoto, *Arch. Ophthalmol.* **107**, 587 (1987)
- [3] R. Birngruber, C. Puliafito, A. Gawande, W. Lin, R. Schoenlein, J. Fujimoto, *IEEE J. Quantum Electron.* **23**, 1836 (1987)
- [4] D. Du, X. Liu, G. Korn, J. Squier, G. Mourou, submitted to *App. Phys. Lett.*

EXHIBIT 2

USSN  
09/775,069

BASIL C. FOUSSIANES  
WILLIAM H. GRIFFITH  
WILLIAM J. WAUGHMAN  
CHESTER L. DAVIS, JR.  
WILLIAM H. FRANCIS  
ROBERT C. COLLINS  
LINDA M. DESCHERE

KEITH D. GRZELAK  
DAVID D. STEIN  
JAMES L. WOLFE

OF COUNSEL  
ROBERT A. CHOATE  
ALFONSE J. D'AMICO

LAW OFFICES OF  
BARNES, KISSELLE, RAISCH, CHOATE,  
WHITEMORE & HULBERT, P.C.

PATENT, TRADEMARK, COPYRIGHT AND  
RELATED INTELLECTUAL PROPERTY LAW  
3800 PENOBSCOT BUILDING  
645 GRISWOLD STREET  
DETROIT, MICHIGAN 48226-4217

TELEPHONE (313) 962-4790  
TELEFAX (313) 962-0158

PRESCOTT M. HULBERT  
1992-1991

LAURENCE J. WHITEMORE  
1971-1948

STUART C. BARNES  
1985-1968

JOHN M. KISSELLE  
1994-1980

ARTHUR RAISCH  
1992-1991

March 31, 1994

VIA FACSIMILE MACHINE

Mitchell A. Goodkin, Esq., P.E.  
Associate Intellectual  
Property Counsel  
The University of Michigan  
Wolverine Tower, Room 2071  
3003 S. State Street  
Ann Arbor, MI 48109-1280

Fax No: (313) 936-1330

Re: 939

Dear Mitch:

I am enclosing a rough draft of the proposed patent application based on the disclosure we received on [REDACTED]. As currently constituted the application covers the various embodiments discussed with you and with the various inventors. I would appreciate it if you would coordinate obtaining review of this proposed draft or advise me as to how you would otherwise like to have this review procedure handled. It is my understanding that one of the inventors, Peter Pronko, may still be in town today so it may be possible to get a draft to him before he leaves.

REDACTED



Mitchell A. Goodkin, Esq., P.E.  
March 31, 1994  
Page Two

**REDACTED**

I look forward to receiving your thoughts and comments on the enclosed material along with comments from the inventors.

Very truly yours,



Linda Deschere  
Robert Collins  
Barnes, Kisselle et al

LD/sc

Enclosures

EXHIBIT 3

tabbies  
USSN  
09/775,069**USL** Ultrafast Science Laboratory

Univer lty of Michigan, IST Bldg., 2200 Boniste I, Ann Arbor, Michigan 48109-2099

Phone: (313) 763-4875

Fax Message

FAX: (313) 763-4876

From:

PETER PRONKO

Date:

3/31

Time: 2:00 PM

To:

LINDA DESCHERE

(Barnes &amp; Kinsella)

Phone:

FAX: 313-962-0158

Number of pages including cover sheet:

6

## Message:

Linda -  
I did not get much time to work on these but  
thought I would send you the quick notes  
appended to the claims. You can discuss these  
with the other inventors to gain some clarification  
if necessary.

Steve

**CUOS****Center for Ultrafast Optical Science**

University of Michigan, IST Bldg., 2200 Bonisteel, Ann Arbor, Michigan 48109-2099

*Jeff*

Fax Message

Call Back Phone (313) 763-4875

Fax Phone (313) 763-4876

From: Jeff Squier/Gérard Mourou

Date: 5 April 1994 Time: 10 AM

To: Linda Deschere  
Barnes, Kisselle

Phone: 313-962-4790

FAX: 313-962-0158

**EXHIBIT 4**

tabbier

USSN  
89/775,069

Number of pages including cover sheet: 78

**Message:**

Jeff Squier's corrections followed by Gérard Mourou's corrections - separated by a sheet of paper.

Please contact Serina Brown @ 313-747-1719 if there are any problems with the transmission of this fax.

EXHIBIT 5

tabbies  
USSN  
09/775,069

BASIL C. FOUSSIANES  
WILLIAM H. GRIFFITH  
WILLIAM J. WAUGHMAN  
CHESTER L. DAVIS, JR.  
WILLIAM H. FRANCIS  
ROBERT C. COLLINS  
LINDA M. DESCHERE

KEITH D. GRZELAK  
DAVID D. STEIN  
JAMES L. WOLFE

OF COUNSEL  
ROBERT A. CHOATE  
ALFONSE J. D'AMICO

LAW OFFICES OF  
BARNES, KISSELLE, RAISCH, CHOATE,  
WHITTEMORE & HULBERT, P.C.

PATENT, TRADEMARK, COPYRIGHT AND  
RELATED INTELLECTUAL PROPERTY LAW

3500 PENOBSCOT BUILDING  
645 GRISWOLD STREET

DETROIT, MICHIGAN 48226-4217

TELEPHONE (313) 962-4790

TELEFAX (313) 962-0158

PRESCOTT M. HULBERT  
1885-1981

LAURENCE J. WHITTEMORE  
1871-1948

STUART C. BARNES  
1885-1988

JOHN M. KISSELLE  
1894-1980

ARTHUR RAISCH  
1902-1981

April 6, 1994

VIA FACSIMILE MACHINE

Mitchell A. Goodkin, Esq., P.E.  
Associate Intellectual  
Property Counsel  
The University of Michigan  
Wolverine Tower, Room 2071  
3003 S. State Street  
Ann Arbor, MI 48109-1280

Fax No: (313) 936-1330

Re: 939

Dear Mitch:

I am sending a second draft patent application on the subject disclosure with modifications per inventors' comments received yesterday and today. I believe I have incorporated all of the modifications suggested, although not necessarily in the same location or form as suggested. The drawings remain informal due to severe time constraints.

**REDACTED**

Mitchell A. Goodkin, Esq., P.E.  
April 6, 1994  
Page Two

**REDACTED**

If there are any questions regarding the "duty of disclosure"  
or any other matter, please let me know.

Very truly yours,



Linda Deschere  
Robert Collins  
Barnes, Kisselle et al

LD/sc  
Enclosures  
CONFIRMATION COPY (Via Federal Express)

cc: Alan Bilinsky (w/out Enclosures)  
Carol Wallace (w/out Enclosures)

**CUOS**

*Center for Ultrafast Optical Science*

University of Michigan, IST Bldg., 2200 Bonisteel, Ann Arbor, Michigan 48109-2099

Fax Message

Call Back Phone (313) 763-4875

Fax Phone (313) 763-4876

From: Gérard Mourou

Date: 7 April 1994 Time: \_\_\_\_\_

To: Linda Deschere

Phone: \_\_\_\_\_

FAX: 313-936-1330

EXHIBIT 6

tabbies  
USSN  
09/775,069

Number of pages including cover sheet:

3

Message:

More corrections.